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Behavior of Organic Pollutants During Rapid-Infiltration of Wastewater Into Soil: II. Mathematical Description of Transport and Transformation

CARL G. ENFIELD, DAVID M. WALTERS, JOHN T. WILSON, and MARVIN D. PIWONI

United States Environmental Protection Agency
Office of Research and Development
Robert S. Kerr Environmental Research Laboratory
P.O. Box 1198, Ada, Oklahoma 74820

ABSTRACT

A compartmental screening model was developed to describe the movement of volatile and transformable organic chemicals in rapid-infiltration wastewater treatment systems. The first compartment describes losses of the chemical from the infiltration basin when the basin is flooded with wastewater. The second compartment considers losses due to volatilization and transformation in near surface soils during periods of drying. The third compartment describes the transport and transformation of the remaining chemical to ground water. The model was developed to consider an accidental spill of chemical into a treatment system or a constant input of chemical into a system. Laboratory data for 18 organic compounds from a microcosm designed to simulate a rapid-infiltration system were used to evaluate the model. Data used in the evaluation were obtained after quasi-steady state had been achieved. No attempt was made in this investigation to evaluate the model's suitability for describing an accidental spill into a treatment system. Projections of volatilization were within a factor of 2 for slowly transformable compounds. The model overestimates volatilization for degradable compounds if one assumes no transformation. When transformation is considered, accounting can be made for chemical losses.

INTRODUCTION

The commercial production of organic compounds has increased steadily during the last forty years. Land treatment and disposal of these chemicals is resulting in the potential transport of hazardous chemicals to ground water. Nevertheless, this problem has been largely ignored principally because of the conception that the natural processes in the soil have an enormous capacity to degrade organic compounds and because of difficulties in trace organic analysis. Recent improvements in analytical methodology for organic pollutants have resulted in observations of widespread pollution of ground water by organic chemicals.

Preservation of the quality of our valuable and irreplaceable soil and ground water resources requires control of the releases of organic chemicals into the soil mantle. To establish control measures that adequately protect our resources yet permit reasonable utilization of the soil as a treatment system, models are needed that describe the transport and transformation of the chemicals in soil systems. The current design guidance given by the U.S. Environmental Protection Agency [1] for land treatment of wastewater does address the problem of potential ground water contamination by trace organic compounds, but does not offer any suggestions on estimating the magnitude of the problem. After indicating limita-

tions of the several existing models, Jury et al. [2] suggested a screening approach for organics in soils, developed to describe pesticide losses, that takes into consideration volatilization. However, Jury's proposed boundary conditions are not totally compatible with rapid infiltration wastewater treatment systems. This investigation was designed to evaluate a screening methodology for predicting transport and transformation of organic chemicals in rapid-infiltration land treatment systems using time variable boundary conditions to simulate the operation of the system and demonstrate, with selected laboratory data, the suitability of the methods for estimating transport through the vapor phase, transport in the liquid phase, and transformation with respect to the liquid and solid phases. The rapid-infiltration land treatment term was adopted to reflect the rate of wastewater application [1]. By definition, any system receiving more than 5.3 m yr^{-1} (4 in wk^{-1}) of wastewater is considered to be rapid infiltration. Water distribution methods and plant cover are quite variable in existing systems. USEPA [1, p. 2-12] recommends a range of estimated design loading for both slow-rate (less than 5.3 m yr^{-1}) and rapid-infiltration land treatment systems directly proportional to permeability of the soil and ranging from 4 to 10 percent of the hydraulic conductivity of the most restrictive layer on an annual average [1, p. 5-19]. The laboratory scale rapid-infiltration land treatment system described applied approximately 16 m yr^{-1} or 5 percent of the saturated hydraulic conductivity with a water table at 1.5 m below the surface (minimum acceptable depth to ground water for rapid infiltration system is 1.2 m [1, p. 2-24].

THEORETICAL DEVELOPMENT

A rapid-infiltration land treatment system's general mode of operation is to apply wastewater to an infiltration basin in two different manners which include: maintaining a constant head of water for a period of time followed by a "resting" or drying period, or applying fixed volumes of water to an infiltration basin either through sprinkler application of surface distribution on fixed wetting/drying cycles. Mathematically, the problem was subdivided into three distinct compartments or cells for a solution where the output from one compartment was the input to the succeeding compartment (Figures 1, 2, 3).

The first compartment was considered to be a surface impoundment which was perfectly mixed and did not consider any losses by infiltration. The chemicals are lost from the compartment by volatilization and/or by hydrolysis. The second compartment was a thin unsaturated soil layer directly beneath the surface impoundment with no water flow and constant water content. The compartment acts to minimize volatile losses to the atmosphere. The chemicals are placed at the bottom of the compartment and loss from the compartment occurred only during the time when there was no water in the surface impoundment. Chemical losses from the compartment are by diffusion to the atmosphere and chemical transformation. The third compartment takes the remaining chemical and transports it through the soil profile assuming a constant water content and constant flux. Chemicals in this compartment are allowed to be transformed assuming first order kinetics. The natural system is a continuum and the conceptual compartmental model is an approximation of this continuum.

Loss From Infiltration Pond

First, consider the wastewater ponded in the infiltration basin. This compartment is intended to describe surface chemical losses during the wetting portion of an operational cycle of the land treatment system. Two major processes are considered--the chemical may be volatilized through the surface of the water and the chemical may be transformed in the bulk of the fluid. If one assumes, in an environmental situation, that the concentration (C) (g/g) of the compound under consideration is small in comparison to the other compounds in the flow system, then we can write:

transformation in liquid phase — liquid to vapor transport

$$dC/dt = -k_{tl}C - k_{vp}C \quad (1)$$

Transformation in the liquid phase assumes first-order kinetics, and $k_{tl}(d^{-1})$ is the rate coefficient. Liquid to vapor transport is assumed to follow Fick's law and $k_{vp}(d^{-1})$ the volatilization coefficient. Following the development of Rathbun and Tai [3]

$$k_{vp} = k_{ol}/L \quad (2)$$

where k_{ol} (m d^{-1}) is the overall mass-transfer coefficient based on the Lewis and Whitman [4] two-film model as reviewed by Mackay et al. [5] and L is the depth of water in the basin (m)

$$1/k_{ol} = 1/k_L + RT/(H\ k_g) \quad (3)$$

where R = the gas constant (8.314 Pa m^3 mol^{-1} K^{-1})
T = absolute temperature (K)
H = Henry's law constant (Pa m^3/mol)
k_L = liquid film transfer coefficient (m/d)
k_g = gas film transfer coefficient (m/d).

Mackay et al. [5] developed an empirical model to describe both the liquid and gas film transfer coefficient under environmental conditions as

$$k_L = 34.1 \times 10^{-6} (6.1 + 0.63\ U_{10})^{0.5}\ U_{10}\ S_{cl}^{-0.5} \quad (4)$$

$$k_g = 46.2 \times 10^{-5} (6.1 + 0.63\ U_{10})^{0.5}\ U_{10}\ S_{cg}^{-0.67} \quad (5)$$

where U_{10} is the ten (10) meter environmental wind velocity (m/s), S_{cl} and S_{cg} are the liquid and gas Schmidt Numbers, respectively. The Schmidt Numbers are obtained from the equation:

$$S_{cm} = \mu_m/(\rho_m D_m) \quad (6)$$

where μ_m is the viscosity of the medium, ρ_m is the density of the medium and D_m is diffusivity of the trace chemical in the medium. Often, data on diffusivity of specific chemicals is limited, and it is necessary to approximate the values from characteristics and reference chemicals. Hwang [6] suggested this could be accomplished for the liquid and gas film transfer coefficients in natural surface impoundments using the equations

$$k_{Li} = (MW_{O_2}/MW_i)^{0.5}\ (T/298)\ k_{LO_2} \quad (7)$$

$$k_{gi} = (MW_{H_2O}/MW_i)^{0.335}\ (T/298)^{1.005}\ k_{gH_2O} \quad (8)$$

where MW is molecular weight (g). The calculations can then be made based on the reference compounds of oxygen and water.

Eq. (1) was solved by substituting the variable

$$k^* = k_{tl} + k_{vp} \quad (9)$$

then, Eq. (1) becomes

$$dC/dt = -k^*C$$

or

$$C = C_0 \exp^{-k^*t} \quad (10)$$

where C_0 is the liquid phase concentration in the pond at the initial time in the operational cycle of the system. Solving Eq. (10) for the time (t) the pond is in existence yields the concentration entering the soil. In the above analysis, it was assumed that the pond did not infiltrate into the soil profile or evaporate from the water surface during its existence, all of the chemical was instantaneously applied to the pond and the depth of the pond was its' average depth during the time present. Since it was assumed that there was no loss of water there is no need to include a convective transport term.

Volatile Losses Between Flooding Cycles

The chemical remaining after losses in the pond was then placed at the bottom of the succeeding compartment which was considered to be an unsaturated soil which could volatilize from the soil surface and degrade in the soil profile.

The soil layer acted as a restrictive layer for volatile losses. It was, therefore, assumed that there was no convective flow through this soil layer and the soil layer was in a quasi-steady state condition. Under these assumptions the distribution of the chemical within the layer can be described by the equation

$$D^* \frac{d^2C_1}{dx^2} - k_t^* C_1 = 0 \tag{11}$$

where D^* is a lumped dispersion coefficient defined in Eq. (32) ($m^2\ s^{-1}$)
x is distance (m)
C_1 is solution concentration referenced to the liquid phase (g/g)
k_t^* is a lumped transformation rate described by Eq. (34) (s^{-1}).

Eq. (11) has the solution

$$C_1 = Ae^{\sqrt{\alpha}\, x} + Be^{-\sqrt{\alpha}\, x} \tag{12}$$

where $\alpha = k_t^*/D^*$ and A and B are constants of integration. Assuming the concentration in the atmosphere just above the soil is zero yields a boundary condition

$$\lim_{x \to 0} C_1 = 0 \tag{13}$$

At the bottom of the compartment the concentration is assumed to be a constant

$$C_1 = C_i \quad \text{at} \quad x = \ell \tag{14}$$

where ℓ is the thickness of the soil layer. With boundary conditions (13), $A = -B$ and Eq. (12) is equivalent to

$$C_1 = 2A \sinh(\sqrt{\alpha}\, x) \tag{15}$$

The chemical flux (J) at $x = \ell$ can be described by the equation

$$J = D^* 2A \sqrt{\alpha} \cosh(\sqrt{\alpha}\ell) \tag{16}$$

Considering conservation of mass

$$CV_d = J(1-FTF) + C_i V_d \tag{17}$$

where C is the concentration remaining after losses in the surface compartment (pond) [from Eq. (10)]. V_d is the Darcy flux of water passing through the third compartment, FTF is the fraction of time flooded (no volatile losses when soil is flooded) and C_i is the concentration entering the third compartment. Substituting

Eq. (15) and Eq. (16) into Eq. (17) yields

$$C_i = \frac{CV_d \sinh(\sqrt{\alpha}\ell)}{(1-FTF)\, D^* \sqrt{\alpha} \cosh(\sqrt{\alpha}\ell) + V_d \sinh(\sqrt{\alpha}\ell)} \tag{18}$$

The boundary condition for this compartment Eq. (14) requires a determination of the thickness of the soil layer through which the chemical is allowed to diffuse. This thickness was assumed to be equal to the travel time for the chemical during one operational cycle of the treatment system (RCT). With this assumption

$$\ell = V_1 \cdot RCT/R \tag{19}$$

where R is a lumped retardation factor defined below [Eq. (31)] and V_1 is the interstitial liquid velocity (m s^{-1}) equal to V_d/θ and θ the volumetric water content (m^3 m^{-3}).

Transport Through Soil Profile

The third compartment describes convective-diffusive transport of a pollutant through soil taking into account processes in the liquid, solid, and vapor phases. If sorption, transformation, and production processes follow first-order kinetics, the liquid phase is assumed to cover all of the solid phase, and transfer from the solid phase to the vapor phase must first pass through the liquid phase then convective-diffusive transport can be described in one dimension by the following three equations:

CHANGE IN LIQUID PHASE

	Dispersive Flux	Convective Flux	Liquid → Solid Transfer

$$\frac{\partial(\theta\rho_1 C_1)}{\partial t} = D_1 \frac{\partial^2(\theta\rho_1 C_1)}{\partial x^2} - V_1 \frac{\partial(\theta\rho_1 C_1)}{\partial x} - k_1 \theta\rho_1 C_1 \tag{20}$$

Solid → Liquid Transfer	Liquid Phase Trans.	Liquid Phase Prod.	Liquid → Vapor Transfer	Vapor → Liquid Transfer

$$+ k_s \rho_s C_s - k_{t1} \theta\rho_1 C_1 + k_{p1} \theta\rho_1 C_1 - k_v \theta\rho_1 C_1 + k_a n \rho_v C_v$$

where C_1 = concentration in liquid phase (g/g)

C_s = concentration in solid phase (g/g)

C_v = concentration in vapor phase (g/g)

D_1 = dispersion coefficient in liquid phase (m^2 s^{-1})

k_a = first order vapor to liquid transfer coefficient (s^{-1})

k_1 = first order liquid to solid transfer coefficient (s^{-1})

k_{p1} = first order liquid phase production (s^{-1})

k_s = first order solid to liquid transfer coefficient (s^{-1})

k_{tl} = first order liquid phase transformation coeffficient (s^{-1})

k_v = first order liquid vapor transfer coefficient (s^{-1})

ρ_l = density of liquid (Mg m^{-3})

ρ_s = density of soil (Mg m^{-3})

ρ_v = density of vapor (Mg m^{-3})

n = air filled porosity (m^3 m^{-3})

CHANGE IN SOLID PHASE

	Liquid → Solid Transfer	Solid → Liquid Transfer	Solid Phase Trans.	Solid Phase Prod.

$$\frac{\partial(\rho_s C_s)}{\partial t} = k_l \theta \rho_l C_l - k_s \rho_s C_s - k_{ts} \rho_s C_s + k_{ps} \rho_s C_s \qquad (21)$$

where k_{ts} = first order transformation in solid phase (s^{-1})

k_{ps} = first order production in solid phase (s^{-1})

and

CHANGE IN VAPOR PHASE

	Dispersive Flux	Convective Flux	Liquid → Vapor Transfer

$$\frac{\partial(n\rho_v C_v)}{\partial} = \frac{D_v \partial^2(n\rho_v C_v)}{\partial x^2} - \frac{V_v \partial(n\rho_v C_v)}{\partial x} + k_v \theta \rho_l C_l$$

Vapor → Liquid Transfer	Vapor Trans.	Vapor Prod.

$$- k_a n \rho_v C_v - k_{tv} n \rho_v C_v + k_{pv} n \rho_v C_v \qquad (22)$$

where D_v = dispersion coefficient in the vapor phase (m^2 s^{-1})

V_v = interstitial vapor velocity (m s^{-1})

k_{tv} = first order transformation in vapor phase (s^{-1})

k_{pv} = first order production in vapor phase (s^{-1})

which leads to :

TOTAL CHANGE

$$\frac{\partial(\theta\rho_l C_l)}{\partial t} + \frac{\partial(\rho_s C_s)}{\partial t} + \frac{\partial(n\rho_v C_v)}{\partial t} = D_l \frac{\partial^2(\theta\rho_l C_l)}{\partial x^2}$$

$$+ D_v \frac{\partial^2(n\rho_v C_v)}{\partial x^2} - V_l \frac{\partial(\theta\rho_l C_l)}{\partial x} - V_v \frac{\partial(n\rho_v C_v)}{\partial x}$$

$$- k_{tl}\theta\rho_l C_l - k_{ts}\rho_s C_s + k_{pl}\theta\rho_l C_l + k_{ps}\rho_s C_s$$

$$+ k_{pv} n\rho_v C_v - k_{tv} n\rho_v C_v \qquad (23)$$

If one assumes local equilibrium exists between the liquid and solid phases, then

$$k_l \theta\rho_l C_l = k_s \rho_s C_s \qquad (24)$$

and one can define a distribution coefficient as

$$k_d \equiv k_l \theta\rho_l / k_s \rho_s \qquad (25)$$

which yields the linear sorption isotherm

$$C_s = k_d C_l \qquad (26)$$

similarly if equilibrium exists between the liquid and vapor phases

$$k_v \theta\rho_l C_l = k_a n\rho_v C_v \qquad (27)$$

and one can define the distribution coefficient

$$k_{dv} \equiv k_v \theta\rho_l / (k_a n\rho_v) \qquad (28)$$

which is the same as a unitless form of the Henry's law coefficient and

$$C_v = k_{dv} C_l \qquad (29)$$

Assuming θ, n, ρ_a, ρ_l, and ρ_s are constant; V_v is zero; production in all phases and transformation in the vapor phase are zero; then Eq. (23) can be rewritten in terms of the liquid phase following the equation:

$$1 + \frac{\rho_s}{\theta\rho_l} k_d + \frac{k_v}{k_a} \frac{\partial C}{\partial t} = D_l + \frac{k_v}{k_a} D_v \frac{\partial^2 C_l}{\partial x^2} - V_l \frac{\partial C_l}{\partial x} - \frac{\rho_s}{\theta\rho_l} k_{ts} k_d + \frac{\theta\rho_l}{\rho_s} k_{tl} C_l \qquad (30)$$

An overall retardation factor (R) can then be defined:

$$R \equiv 1 + \frac{\rho_s}{\theta\rho_l} k_d + \frac{k_v}{k_a} \qquad (31)$$

and an effective dispersion coefficient (D*) as :

$$D^* \equiv D_l + \frac{k_v}{k_a} D_v \tag{32}$$

Millington and Quirk [7] related diffusion in air-filled pores to the air-filled porosity (η) and the total porosity (P_t) to account for the tortuosity of the pores on vapor transport using the equation:

$$D_v = D_0(\eta^{10/3}/P_t^2) \tag{33}$$

where D_0 is diffusion coefficient of the chemical in air and D_v is effective dispersion coefficient in vapor phase ($m^2\ s^{-1}$) Sallam, et al. [8] evaluated this approach and found it to more closely describe the effective diffusion coefficient than other models in the literature. A lumped first-order transformation term (k_t^*) can be defined as

$$k_t^* \equiv k_{ts}k_d + \frac{\theta\rho_l}{\rho_s} k_{tl} \tag{34}$$

Eq. (30) has been solved for a variety of boundary conditions (van Genuchten and Alves, [9] when one defines the transformation coefficient (μ) as:

$$\mu = \rho_s k_t^*/\theta\rho_l \tag{35}$$

The initial and boundary conditions which appear to approximate a rapid-infiltration land treatment system are

$$C_l(x,0) = C_{in}$$

$$- \quad C_i \text{ for } 0<t\leq t_o$$

$$C_l(0,t) =$$

$$0 \text{ for } t>t_o$$

$$\partial C_l/\partial x\ (\infty,t) = 0$$

where t_o is the total time the chemical is applied to the land treatment system and C_{in} is the initial concentration throughout the profile which has the solution

$$C_l(x,t) =$$

$$C_{in}A(x,t) + C_iB(x,t) \qquad 0<t\leq t_o$$

$$C_{in}A(x,t) + C_iB(x,t) - C_iB(x,t-t_o) \qquad t>t_o$$

where

$$A(x,t) = \exp(-\mu t/R)\left[1 - 1/2\ \mathrm{erfc}\ \frac{Rx - V_1 t}{2(D^*Rt)^{1/2}}\right.$$

$$\left. -1/2\ \exp\ (V_1 x/D^*)\ \mathrm{erfc}\ \frac{Rx + V_1 t}{2(D^*Rt)^{1/2}}\right]$$

$$B(x,t) = 1/2\ \exp\ \frac{(V_1-u)x}{2D}\ \mathrm{erfc}\ \frac{Rx - ut}{2(D^*Rt)^{1/2}} \qquad (36)$$

$$+ 1/2\ \exp\ \frac{(V_1+u)x}{2D^*}\ \mathrm{erfc}\ \frac{Rx + ut}{2(D^*Rt)^{1/2}}$$

$$\text{and } u = V_1\ \left[1 + \frac{4\mu D^*}{V^2}\right]^{1/2}$$

It should be noted that the coordinate system for a solution to Eq. (36) is displaced from the surface by the distance ℓ (Eq. 19) used in calculating the volatile losses between flooding cycles.

MODEL EVALUATION

A solution to Eq. (10) requires knowledge of the compounds molecular weight, temperature of the water, wind speed, and Henry's law constant. Frequently, data are not available for the Henry's law constant, and it must be estimated. Dilling [10] proposed describing the unitless vapor-liquid distribution coefficient using an equation based on water solubility vapor pressure, temperature and molecular weight. Adapting Dilling's equation to the SI systems yields

$$k_{dv} = 2138.\ P(MW)^2/TS \qquad (37)$$

where S = solubility in liquid (mol m^{-3})
P = vapor pressure (Pa)
MW = molecular weight (g).

This approach was used consistently to make all projections. Table 1 lists the projected Henry's law constant along with selected values obtained from the literature. The projected values appear to be reasonably adequate.

The wind speed in the microcosm used in this study was not measured. The volume flow rate of 1 $m(m)^3\ min^{-1}$ (1 L min^{-1}) is equivalent to an air exchange every 8 min. in the "greenhouse" above the column. The calculations in Eqs. (4) and (5) assume a U_{10} wind speed of 0.1 m/s. This is considerably greater than the wind speed in the column, but it was felt to be an adequate approximation due to the way the air was being swept from the "greenhouse." Changing the assumed wind speed to 10^{-6} m/s does not change the resultant projected volatile losses by more than 20% under the experimental conditions. In the second compartment, the concentration was assumed to be zero at the soil surface [Eq. (13)]. Due to the upward flow rate this assumption appears reasonable.

The chemical properties for the compounds added to the wastewater, required to evaluate the loss from ponded water, are given in Table 1. As described in the companion paper (Piwoni, et al., [11]), 0.733 cm of wastewater was applied to the columns once every 4 hours [4 hr = RCT in Eq. (19)]. All the water was applied essentially instantly and disappeared in approximately 0.4 hr [0.4 hr = t in Eq. (10)]. The maximum depth of the water would be 0.73 cm. An average depth

TABLE 1.
Physical/Chemical Properties of Applied Organic Compounds

Compound	Molecular Weight	Water Solubility	Vapor Pressure	log K_{ow}	k_d §§	Henry's Law Constant		Transformation coefficients			Volatilization C/C0	
						Calc	Literature ¶ @298K	k_{t1} ¶	Literature μ	Observed ††	Measured	Predicted†††
	g	mol m^{-3} @Temp K	kPa @298K			kPa m^3 mol^{-1}		d^{-1}				
Halogenated aliphatic hydrocarbons												
Chloroform	119.38	65.67*	25.6§	1.97	0.041	0.39	0.38±0.03§	0.0015	<0.008¶¶	<0.1	0.75±.19	0.42
1,1-dichloroethane	98.96	51.54*	30.10§	1.79	0.033	0.58	0.58±0.02§	0.006		<0.1	0.54±.15	0.54
1,1,1-trichloroethane	133.41	5.40*	16.5§	2.17	0.052	3.00	2.8±0.04§	0.006		<0.1	0.89±.20	0.97
1,2-dibromo-3-chloropropane (DBCP)	236.	2.54**	0.1@293K#	1.28	0.018	0.039	0.061***	N.D.††		0.3	0.43±.14¶¶¶	0.06
Trichloroethene (TCE)	131.5	8.37*	8.0@293K§	2.29	0.060	0.96	0.939@293K§	0.0022		<0.1	0.77±0.33	0.77
Tetrachloroethene (PCE)	165.83	0.90@298†	2.4§§	2.28	0.060	2.76	2.3±0.4	0.0026	0.023-0.0023¶¶	<0.1	0.96±0.72	0.99
Substituted benzenes												
Chlorobenzene	112.56	4.44@293†	1.573†	2.84	0.116	0.35	0.35±0.05§	N.D.	0.023-0.0023¶¶	8.	0.14±.07	0.51
1,2-dichlorobenzene	147.01	0.89@298†	0.196§	3.38	0.222	0.20	0.19±0.01§	N.D.	0.023-0.0023¶¶	>8.	0.21±.12	0.43
1,2,4-trichlorobenzene	181.46	0.17@298†	0.0606§	4.26	0.638	0.36	0.38§	N.D.	0.023-0.0023¶¶	>8.	N.D.	0.89
Nitrobenzene	123.1	15.43@293†	0.02@293K†	1.85	0.036	1.30×10^{-3}		N.D.	<0.023¶¶	>8.	N.D.	0.002
Toluene	92.13	5.59@293†	3.80§	2.69	0.097	0.68	0.670±0.035§	N.D.		1.	.2±.18	0.72
Phenols												
Phenol	94.11	871.32@288†	0.02@293K†	1.46	0.022	0.023×10^{-3}		N.D.	4.8-6.2##	15.	N.D.	<0.001
2-chlorophenol	128.56	202.24@293†	0.29@293K†	2.17	0.052	1.4×10^{-3}		N.D.		>15.	N.D.	0.002
2,4-dichlorophenol	164.01	27.44@298†	0.02@293K†	2.75	0.105	0.72×10^{-3}		N.D.		>15.	N.D.	0.001
2,4,6-trichlorophenol	197.46	4.05@298†	0.13@350K†	3.38	0.222	0.032		N.D.		>15.	N.D.	0.094
Miscellaneous compounds												
Diethylphthalate	222.2	4.03@298†	0.007@343K†	3.22	0.184	1.74×10^{-3}		N.D.			N.D.	0.005
2-chloroethylvinyl ether	106.35	141.06¶	3.56@293K¶	1.28	0.018	0.025		0.37×10^{-4}		0.9	0.47±.26¶¶¶	0.03
Bis(2-chloroethyl) ether	143.02	71.32†	0.19†	1.58	0.026	$2.66E^{-3}$		0.06		0.1	N.D.	0.03

§§ Calculated from relationship between k_{ow} and k_{oc} proposed by Briggs [12]
¶¶ Adapted from Zoeteman et al. [22]
Adapted from Scott, Wolf, and Lavy [20]
*** Cohen et al. [27]
††† The predicted volatilization ignores any potential transformation
¶¶¶ The measured amount volatilized includes other chemicals which coeluted with the study compound

* Adapted from Dilling [10]
** S. Z. Cohen personal communication, Office of Pesticide Programs, U.S. EPA, Washington, DC
† Verschueren [23]
¶ Callahan et al. [29]. K_{t1} is taken as the reported rate of hydrolysis
§ Mackay & Shiu [25]
# Jolles [26]
†† N.D. indicates no data or below detectable limits
‡‡ Best fit value to match measured observed steady state concentrations in soil columns
†† Best fit value to match measured observed steady state concentrations in soil columns

during the 0.4 hours when the pond was present was assumed to be 0.3 cm and used for L in Eq. (2), to calculate the volatilization coefficient. The 0.3 cm was selected considering the Phillips infiltration equation.

To solve Eq. (18) or Eq. (36) requires a knowledge of the distribution coefficient in Eq. (25). This is normally obtained by measuring sorption isotherms. Numerous researchers have proposed approximating the distribution coefficient based on the water solubility of the compound or the octanol/water partition coefficient and the amount of organic carbon in the soil (i.e., Briggs [12], Brown & Flagg [13], Chiou et al. [14], Griffin et al. [15], Karickhoff et al. [16], Kenaga and Goring [17], Means et al. [18], and Schwarzenbach and Westall [19]. In this development, the distribution coefficient (K_d) listed in Table 1 was used to determine the retardation factor (Eq. 31) based on the work of Briggs [12] following the equation

$$\log K_d = 0.52 \log K_{ow} + 0.65 + \log F \qquad (38)$$

where K_{ow} is the octanol/water partition coefficient and F is the fraction of organic carbon in the soil.

Included in Table 1 are values for rate coefficient μ of Eq. (35). The value listed in the table is a value eye fit to the experimental data as observed after quasi-steady-state conditions have been achieved. There are very few data in the literature to describe biotransformations. Scott et al. [20] reported first-order degradation rates on two soils for phenol of 0.26 and 0.198 hr^{-1}. These rates are consistent with observations in this study (Table 1) and are significantly greater than a rate of 2×10^{-3} hr^{-1} reported by Rees and King [21]. However, Rees and King [21] used much higher concentrations of phenol than this study and the study reported by Scott et al. [20]. Transformation rates for several compounds of interest were discussed by Zoeteman et al. [22] from a field study and listed in Table 1. The rate coefficient is an overall loss rate coefficient for ground waters which would include both transformation and volatile losses. The rate coefficient, μ, is only a portion of the overall loss rate coefficient. Thus, the total rate reported by Zoeteman et al. [22] is not consistent with μ used in the model development and is listed only for comparative purposes.

The confidence levels of the rate coefficient determined in this study is low since an assumed model was used to determine the rate coefficients and daughter products were not quantified and the results should be considered semiquantitative. There was too much variability in the experimental data or insufficient replications to minimize the impact of this variability and make the results truly quantitative. Figs. 4-9 show both experimental data and projected concentrations. The figures show a quasi-steady-state condition. The impact of the rate coefficient on the projected concentration in the soil solution is presented when the rate coefficient is believed to be significant. In general, there is good agreement between the measured amount lost to volatilization and the amount predicted. In Fig. 4 and 5, there is no measurable transformation. Thus, in Fig. 4 and 5 there is no fitting of the data used in the proposed compartmental model. The theoretical results shown are strictly based on independent observations of chemical properties and physical properties at the flow system.

Toluene (Fig. 6) apparently degrades. Tobak et al. [28] reported rapid degradation in a culture medium with no attempt made to quantify the results. To be consistent with the experimental observations, rapid degradation would need to occur down to some "threshold" concentration of about 0.1 times the applied solution concentration or 0.3 µmol/L and then stop; otherwise, the concentrations in the soil would continue to decrease as a function of depth. A threshold concentration for biological adaption has been suggested by Boethling and Alexander [29] but was not considered in the development of the model.

Significant transformations were observed with 2-chloroethylvinyl ether but the experimental data shown in Fig. 7 are not consistent with first-order kinetics. The order of the reaction appears to be close to 1.7. The model development was based on an assumption of first-order kinetics; therefore, the projected curve does not follow the experimental data. The behavior of bis(2-chloroethyl) ether

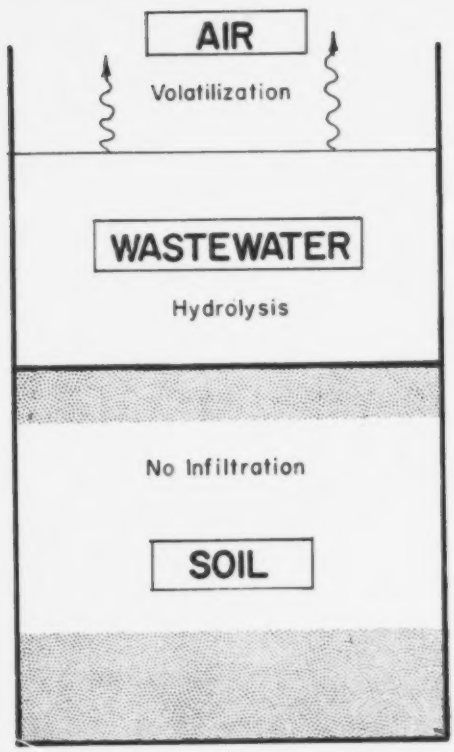

FIGURE 1. First Compartment of Model - Wastewater Impounded on Surface.

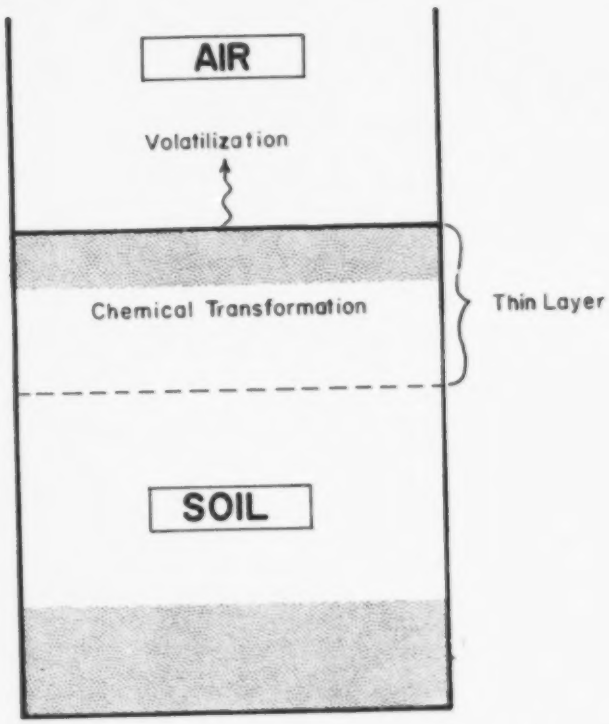

FIGURE 2. Second Compartment of Model - Wastewater Moves into Thin Layer of Soil.

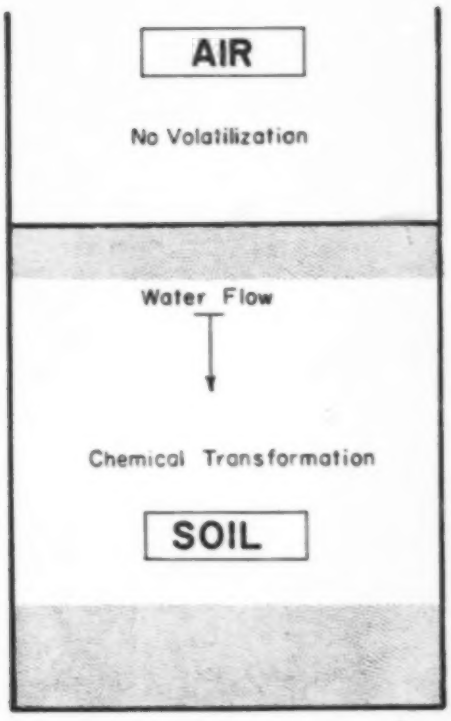

FIGURE 3. Third Compartment of Model - Wastewater is Transported Through Soil Profile.

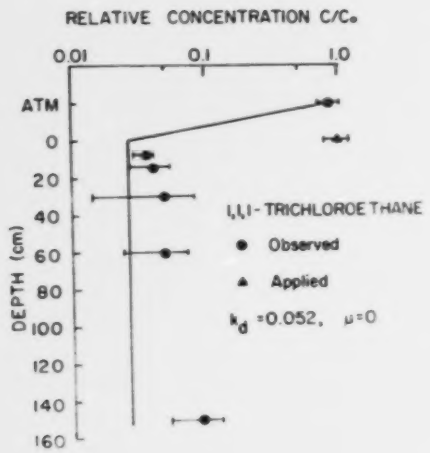

FIGURE 4. Relative Concentration of 1,1,1-Trichloroethane as a Function of Depth

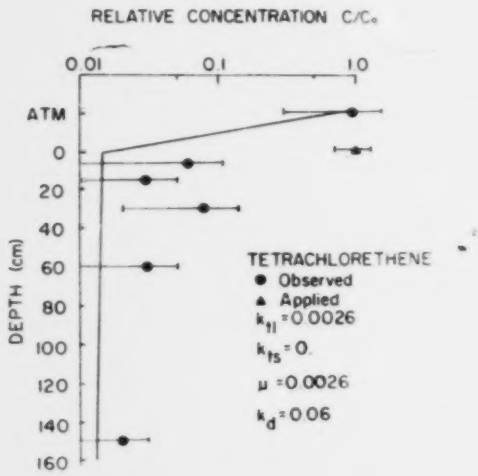

FIGURE 5. Relative Concentration of Tetrachloroethene as a Function of Depth

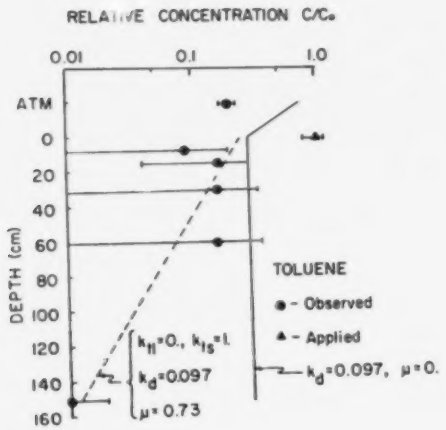

FIGURE 6. Relative Concentration of Toluene as a Function of Depth

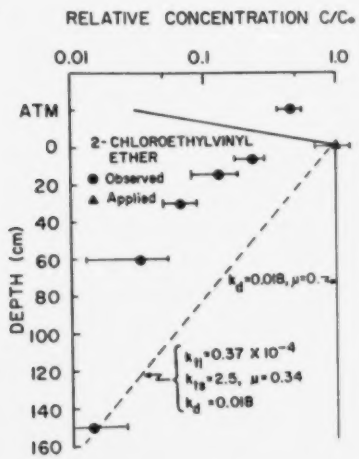

FIGURE 7. Relative Concentration of 2-Chloroethylvinyl Ether as a Function of Depth
NOTE: The 2-chloroethylvinyl ether reported in the atmosphere includes significant concentrations of an unidentified volatile degradate from the original wastewater. This is documented by [11].

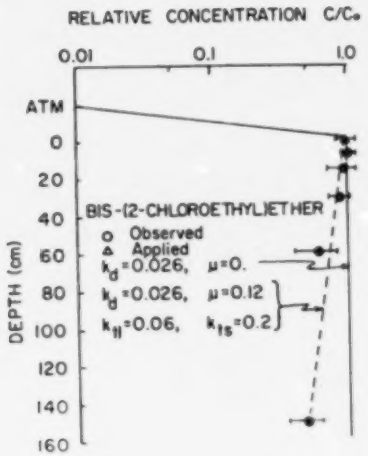

FIGURE 8. Relative Concentration of Bis (2-Chloroethyl) Ether as a Function of Depth.

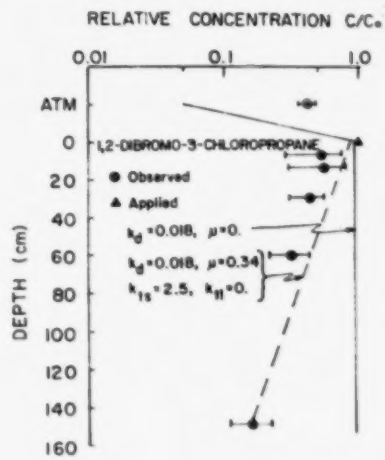

FIGURE 9. Relative Concentration of 1,2-Dibromo-3-Chloropropane (DBCP) as a Function of Depth. NOTE: Ethyl benzene, a volatile compound, coeluted with DBCP. Ethyl benzene-DBCP was found in the atmosphere above the soil columns at approximately the same concentration in columns where no DBCP was added as those columns where DBCP was added. No ethyl benzene-DBCP was detected below the soil surface when DBCP was not added to the wastewater.

as shown in Fig. 8 indicated transformation appears to follow first-order kinetics. If k_{ts} was assumed to be equal to zero, the projected curve would be within the error bars of the experimental data indicating hydrolysis may be the only transformation process. DBCP also showed significant transformation (Fig. 9). The rate coefficient observed is significantly greater than the reported rate of hydrolysis. In agricultural soils, DBCP is reported to degrade over several weeks [27]. This is of the same magnitude as the 0.3 d^{-1} observed.

The remainder of the compounds are not shown graphically. A summary of the observed rate coefficients are listed in Table 1. Figure 10 is a plot of the measured fraction volatilized versus the projected fraction volatilized. The volatilization projected assume no transformation in this figure. The project volatilization includes no "curve fit" parameters. All of the observed compounds are included in the figure. Those compounds where there was apparent transformation (concentration remaining after volatilization greater than concentration observed at the effluent of the column) are shown with a solid square and those compounds where there was little or no transformation by a circle. The agreement between projected and measured volatilization is good when there is little transformation. Where necessary, the rate coefficient μ in Table 1 is listed as greater than or less than values. Any numerical value for μ is based on the analytical detection limits for the compounds and k_d, or on the ability to observe a gradient in the concentration as a function of depth. The transformation rate coefficient observed was frequently greater than other reported values. One can hypothesize the higher transformation rates seen in this study may be due to presence of wastewater containing an ample supply of mineral nutrients (particularly N and P) enabling the organisms to maintain a high rate of metabolism.

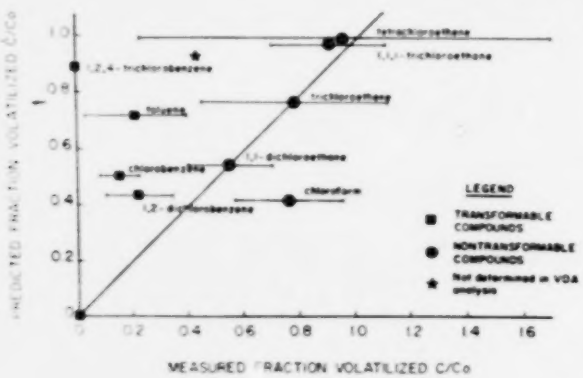

FIGURE 10. Measured Relative Volatilization vs. Predicted Relative Volatilization.

CONCLUSIONS

A process oriented compartmental screening model has been proposed and evaluated which is suitable for determining the potential contamination of ground water due wastewater application to rapid-infiltration wastewater treatment systems. The model may be suitable for other land treatment systems but due to the assumed artificial boundary conditions, it should not be applied before the model is evaluated with experimental data. The transformation rate coefficients, a fitted parameter in this study, were consistently greater than those reported in the literature. For volatile chemicals which were slowly transformed, the projected concentrations were in good agreement measured values. This suggests the model can be used to describe potential volatile losses based strictly on chemical properties and the operating constraints of the treatment system. A major limitation to implementation of the model in design practice is lack of knowledge on

transformation rates. Where data were available in the literature for chemical transformation rates, model projections would yield a higher chemical concentration in the soil solution than observed with the experimental data.

ACKNOWLEDGEMENTS

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Address reprint requests to:
Dr. Carl G. Enfield
U.S. Environmental Protection Agency
R.S. Kerr Environmental Research Laboratory
P.O. Box 1198
Ada, OK 74820

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